A New Molecular Model for Water Adsorption on Graphitized Carbon Black

by

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Abstract

Adsorption of water on graphitized carbon black at various temperatures has been studied with a new molecular model of graphitized carbon black using Monte Carlo simulation. The model is a collection of graphene layers, modelled by the Steele potential, and a number of phenol groups forming clusters of various sizes which are placed randomly at the graphene edge sites to give an O/C ratio of 0.006. The results are compared with experimental data reported by Kiselev *et al.* [1] in 1968 for a range of temperatures, and for the first time a reconciliation between the experimental data and simulation has been successfully achieved. The simulation results show that water adsorbs preferentially around the functional groups to form clusters, which then grow and merge at the edges of the graphene layers, rather than adsorbing onto the basal planes of the graphene because the electrostatic interactions (hydrogen bonding) between water molecules are stronger than the basal plane-water dispersion interactions.

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1. Introduction

The unique behaviour of water has been an intriguing challenge to experimentalists and theoreticians studying this ubiquitous liquid for many decades. The unusual behaviour of water is, to a large extent, a consequence of the very strong electrostatic interaction between the positively charged hydrogen atoms and the lone pair on the oxygen giving rise to strongly directional hydrogen bonds linking the molecules. The earliest simulation study of water was made by Rahman and Stillinger in 1971 [2] who used the tetrahedral BenNaim and Stillinger model [3] with four partial charges at its corners to represent the negative lone pair on oxygen and the positive charges on the hydrogen atoms and a dispersive repulsive term equivalent to the isoelectronic neon atom. Most subsequent water models have been variants of this pattern, the most radical departure being the replacement of the two lone pair charges by a single charge, positioned so that the effective dipole maintains the tetrahedral network characteristics of the fluid.

Adsorption of water on carbon surfaces has been the subject of many experimental studies since the pioneering study of a highly graphitised adsorbent by Kiselev and co-workers in 1968 [1]. The topic is of particular practical interest because of its implications for the use of carbon adsorbents in separation processes where the presence of small amounts of water can be of crucial importance. For example, in the removal of volatile organic compounds (VOCs) from air, the carbon adsorbent capacity for VOCs may be severely reduced by the presence of water [4], despite the hydrophobic character of the carbon surface.

In its pure graphitic form, carbon should have only a very weak interaction with water, since the attractive part of the interaction is primarily through dispersion forces and because these are neon-like, they contribute only a very small holding potential at ambient temperatures.

Although later models attributed a higher polarizability to the water molecule than that of neon, the dispersion interaction with a purely graphitic surface remains very small.

The observation that water is adsorbed strongly at low relative pressures by carbon adsorbents has prompted a number of simulation studies. One possible explanation is that the potential overlap in very narrow pores, which deepens the potential well by a factor of two or more, may be responsible, and several simulation studies have explored this possibility [5-10]. Nguyen and Bhatia [11], using a reconstructed carbon model, showed that water clusters can grow from a nucleus trapped in an extremely narrow space, as has also been demonstrated in a more formal model [8].

Chemical heterogeneities [12], specifically functional groups attached to the surface [13-18] have also been invoked as an explanation of the experimental observations. Partial charges on these groups interact strongly with the charges on the water molecules, and more water molecules can then be added to form clusters around the functional groups. In many simulations studies, the functional groups have been attached to the graphene surface. However, theoretical considerations suggest that attachment to the surface is improbable, and that the dangling bonds at edge sites, leading to strongly localised charge density are a more probable location for functional groups [19-23], or indeed that the edge charges themselves may be sufficient to nucleate water adsorption [24-26].

In the case of highly graphitised carbons, explanations of the observed isotherms based on narrow pores can clearly be ruled out, nevertheless these adsorbents exhibit strong water uptake [1] in the form of type III isotherms. It might be argued that graphitisation at extremely high temperature (approaching 3000K) would destroy or remove most functional

groups as well as reducing particle size and surface area. However the very large number of edge sites per particle is likely to ensure that residual electrostatic charge will be present at the edges.

In this study we propose a new molecular model for graphitized carbon black (GCB), with phenol groups forming clusters of various sizes and fixed at the edge sites of the stacked graphene layers that make up the adsorbent, in order to study water adsorption at various temperatures. Phenol groups were chosen because, according to Morimoto and Miura [19, 20], heat treatment at temperatures above 1000^{o}C removes all carboxyl groups from the carbon surface, but leaves a detectable residue of phenol groups. Our simulation results are compared with the experimental data of Kiselev and co-workers [1].

2. Potential Models

2.1 *Fluid Potential Model*

The rigid non-polarizable polyatomic SPC/E model [27] was used to model water. The model has a single LJ site located at the centre of the oxygen atom and three fixed point charges representing the charge distribution of the molecule. Two positive charges (q^{+}) are located at the centres of the hydrogen atoms, and a single negative charge (q^{-}) is located at the centre of oxygen atom. The molecular parameters of this model are given in Table 1Table 1. The Lennard-Jones 12-6 potential was employed to describe the pairwise fluid-fluid interaction energy.

Table 1. SPC/E model parameters [27]

Parameter	SPCE
ε_{OO}/k_b (K)	78.23
σ_{OO} (nm)	0.3166
R_{OH} (nm)	0.1
$\angle_{HOH}$ (deg)	109.47
q^{-} (e)	0.8476
q^{+} (e)	0.4238

The vapour-liquid equilibrium properties of the SPC/E potential model were taken from NIST for a number of temperatures and are given in Table 2Table 2. To calculate the vapour pressure at other temperatures we used the Antoine equation $ln(P_0) = B - A/T$ to fit the NIST data and interpolated the results. The saturated vapour densities at other temperatures were calculated using the ideal gas equation of state, while the saturated liquid densities were computed using the following equation [28]:

$$\rho_2^L = \frac{\rho_1^L}{1+\beta(t_2 - t_1)} \quad (1)$$

where β is the coefficient of volumetric thermal expansion of water (β=0.000214$^oC^{-1}$)

Table 2. Saturation properties of SPC/E water model at various temperatures[a]

Parameter	**Unit**	**NIST data**				**Interpolation**			
		300K	**350K**	**400K**	**450K**	**302K**	**313K**	**316K**	**323K**
P^{VAP}	kPa	1.04	16.3	117.1	520.0	1.30	2.45	2.89	4.20
ρ^V	mol/m^3	0.42	5.72	37.1	156.7	0.52	0.94	1.1	1.56
ρ^L	mol/m^3	55384	53556	51111	47944	55359	55229	55193	55111

2.2 *Adsorbent Model*

The model for GCB with phenol groups was constructed as follows: First, we constructed two parallel graphene layers, each of which consisted of 2800 carbon atoms with x- and y-dimensions of 8.61nm x 8.52nm. They were positioned to be offset from each other as shown in Figure 1a by cyan and grey colors representing the carbon atoms of the 1st and 2nd layers, respectively. In each layer the carbon atoms were arranged in a regular hexagonal array separated by 0.142nm with a space between the layers of 0.335nm. 23 OH groups were then added at the edge sites of each graphene sheet so that the separation between two adjacent groups in each layer was approximately 1.23nm (Figures 1b and 1c) and phenol

[a] Linstrom PJ, Mallard WG. NIST Chemistry WebBook. 2001 [cited; Available from: http://webbook.nist.gov.

groups in the 2nd layer were offset with those of 1st layer. Finally the model solid was constructed from 15 graphene layers, by the addition of a further 13 layers which were replicas of the first two layers as illustrated in Figure 1d.

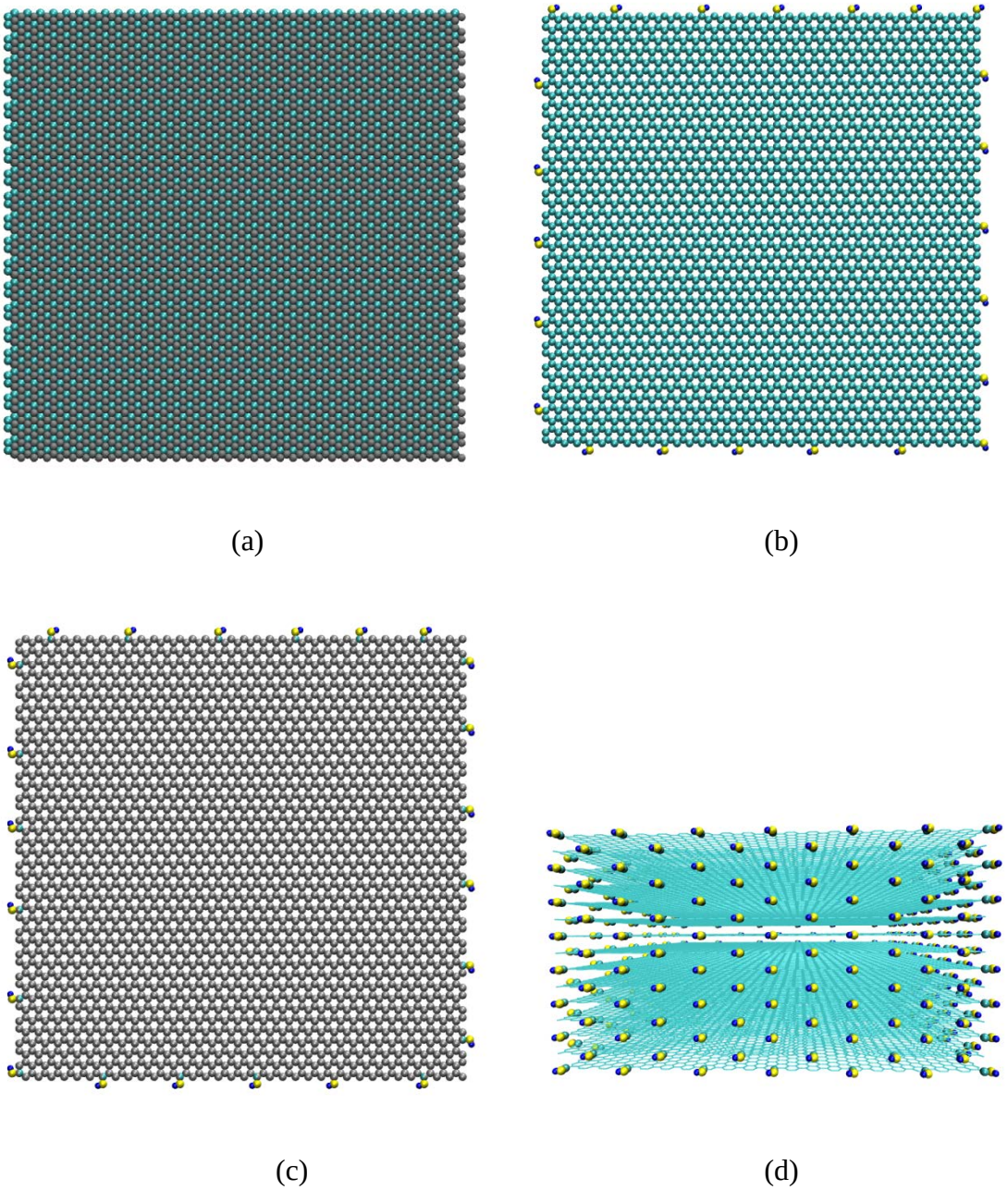


Figure 1: (a) carbon configurations of the first two graphene layers: carbon atoms of 1st layer (cyan) and 2nd layer (grey); (b) arrangement of phenol groups in the 1st layer; (c) arrangement of phenol groups in the 2nd layer; (d) side view of 15 graphene layers with phenol groups fixed at edge sites: carbon (cyan); oxygen (yellow) and hydrogen (blue)

A number of OH groups were then removed at random to leave 250 phenol groups remaining at the graphite edges (Figure 2). The O/C ratio of this solid model is equal to 0.006. This is in close accord with studies by Larsen *et al.* [29] who used X-ray photoelectron spectroscopy (XPS) to determine the oxygen content of a series of carbon blacks (CB) and reported that for CB heat-treated at 3000°C the ratio of O/C was 0.005. Figure 2b, shows that after random removal of OH, the phenol groups tend to form clusters of various sizes at the edge sites of graphite.

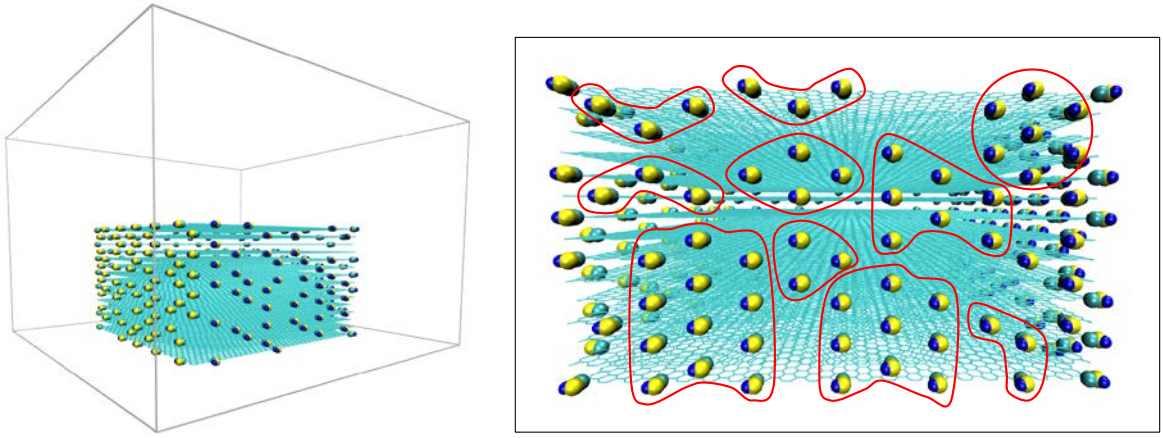


Figure 2: Schematic diagram: (a) simulation box with the new solid model; (b) one edge side of graphite with clusters of fixed phenol groups: carbon (cyan); oxygen (yellow) and hydrogen (blue)

The solid-fluid potential energy of the LJ site in a water molecule *i* and the basal plane of the surface were calculated by Steele 10-4-3 potential equation [30]:

$$\varphi_i^{surf} = 2\pi\rho_s\varepsilon_{os}\left(\sigma_{os}\right)^2\left[\frac{2}{5}\left(\frac{\sigma_{os}}{z_i}\right)^{10} - \left(\frac{\sigma_{os}}{z_i}\right)^4 - \left(\frac{\sigma_{os}{}^4}{3\Delta\left(z_i + 0.61\Delta\right)^3}\right)\right] \quad (2)$$

where φ_i^{surf} is the interaction energy between a water molecule *i* and the carbon surface, ρ_s is the carbon surface density of the graphene layer (38.2 nm^{-2}), Δ is the separation distance between graphene layers (0.335nm), z_i is the separation of the water's LJ site and the uppermost surface layer and ε_{os} and σ_{os} are the cross LJ-well depth and cross collision diameter, respectively, between the LJ site on water and the carbon atom calculated using the Lorentz-Berthelot mixing rule [31].

$$\sigma_{os} = (\sigma_{ss} + \sigma_{oo})/2 \quad (3a)$$

$$\varepsilon_{os} = \sqrt{\varepsilon_{ss}\varepsilon_{oo}} \quad (3b)$$

The LJ parameters used for a carbon atom in a graphene layer are σ_{ss}=0.34nm and ε_{ss}/k_B = 28K following Crowell [32] who matched the interaction energy between basal planes of graphite to the compressibility of graphite in the direction perpendicular to this plane. This procedure gives a minimum in the interaction energy between water and graphite of -6.82 kJ/mol.

The graphite surface was positioned in the middle of one face of the simulation box, normal to the z-direction at a distance from the edge of the surface to the edge of the simulation box of 10σ (Figure 1a), where σ is the collision diameter of oxygen atom of water, thus ensuring that enough room is available for water molecules to form clusters around the solid. The box height was chosen to be large enough (L_z = 30σ) for the opposite face to be modelled as a hard wall. If the centre of the LJ site on water was outside the surface in the x- and y-directions, its interaction with the solid was set to zero.

2.3 *Functional groups.*

The carbon, oxygen and hydrogen atoms of the phenol group were positioned in the same plane as the graphene layer (Figure 3). This arrangement is an idealised representation of the heterogeneity of the surface and can promote adsorption of water on the surface.

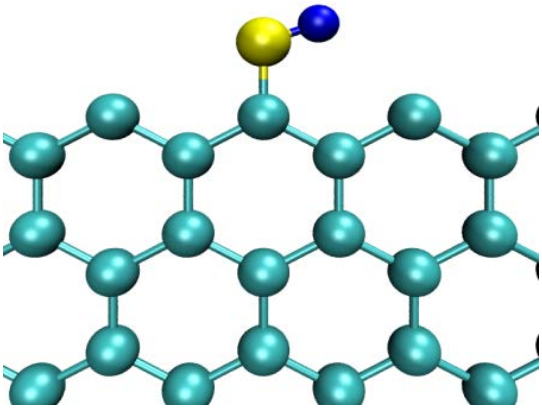


Figure 3: Projection of phenol group attached to the edge of graphene layer: carbon (cyan); oxygen (yellow) and hydrogen (blue)

The parameters for the phenol groups were taken from potential models for the phenol molecule [33] and are given in Tables 3 and 4. The cross LJ parameters between fluid molecules and the functional groups are calculated using the Lorentz-Berthelot mixing rule [31]. The interaction energy between a water molecule and a functional group was calculated from the Lennard-Jones 12-6 potential and an electrostatic Coulomb equation. The surface of real carbon blacks may contain different types of functional groups as well as electrostatic charges due to the edge site configuration of electrons, whose interaction with water may differ from that of the phenol. Moreover, the partial charge of an OH attached to a graphene sheet may be modified from that of free phenol. To accommodate these possibilities we introduce a factor, *F*, to moderate the average interaction between fluid molecule and the phenol groups. We have found that a value of F = 1.125 gives the best description of the experimental data.

The water-phenol group potential used in the simulation, is therefore written as

$$\Phi_{i,j} = F\varphi_{i,j} \tag{4}$$

where $\varphi_{i,j}$ is the interaction energy between a water molecule *i* and a phenol group *j*.

Table 3. Interaction parameters of phenol group

Site	σ (nm)	ε/k_b (K)	q (e)
C[a]	-	-	0.2
O	0.307	78.2	-0.64
H	-	-	0.44

[a] Carbon located in plane of graphene sheet.

Table 4. Phenol site separations and angles

Bond	R (nm)	<	Angle (°)
C[a]-O	0.1364		
O-H	0.096	C[a]OH	110.5

[a] Carbon located in plane of graphene sheet.

3. Simulation Details

Monte Carlo simulations were conducted in the grand canonical ensemble [31]. The chemical potentials used in the simulations were those for an ideal gas; a reasonable approximation for the low pressures in this paper. Simulations were conducted at temperatures ranging from 302K to 323K, corresponding to those measured in the experiments of Kiselev et al. [1]. Each simulated isotherm point was equilibrated until the number of molecules and the energy of the system had converged. Typically this required a minimum of 2.5×10^7 and up to 6×10^9 Monte Carlo steps, depending on the position on the isotherm. Final configurations were used as the initial configuration for the next pressure, mimicking the experimental adsorption procedure.

No long-range corrections were applied for either dispersion (LJ) or electrostatic interactions. Long range corrections for the Coulomb interactions, for example the technique of Heyes and

Van Swol [34, 35], or a two dimensional (2D) Ewald-type sum [35, 36] greatly increase the computation time required to achieve convergence. Shevade et al. [37] have reported a small difference in the adsorption potential between systems where a 2D Ewald-type sum was used and ones where it was omitted. They found that the 2D Ewald sum method increased the computation time by two orders of magnitude, compared to using a half-box length cut-off, and therefore did not apply this correction in their reported calculations. Later simulations of water in carbon pores have also followed this practice [6, 9, 13, 38-40]. In this work we used a cut-off for the LJ and Coulomb interactions equal to half of the simulation box length.

In this work surface excess was calculated with the following equation:

$$\Gamma_{ex} = \frac{\langle N \rangle - \rho_G V_{acc}}{S} \tag{5}$$

where ρ_G is the bulk molecular density, S is the surface area of the solid, <N> is the ensemble average of the number of particles in the simulation box, and V_{acc} is the accessible volume [41].

4. Results and Discussion

There are very few experimental studies of water adsorption on highly graphitised carbon black. The term "highly graphitised" refers to a carbon black which has been heated to a temperature of 2700K or higher under vacuum, or in a reducing environment of pure hydrogen. Three studies of water adsorption on graphitised carbon black were carried out by Kiselev et al. [1], Easton and Machin [42] and Tarasevich et al. [43]. Amongst these, the one by Kiselev and co-workers is of most interest to us because their isotherms are more extensive and suitable for comparison with simulation results. Furthermore, the carbon black used in their study was one of the most energetically homogeneous carbon blacks ever prepared. It was heat treated to 3273 K, had no detectable micropores, a very flat and large

basal plane of graphite, and a correspondingly low nitrogen surface area of 7.6m^2/g. The experimental isotherm at 302.15 K, from Kiselev *et al*. [1], is reproduced in Figure 4.

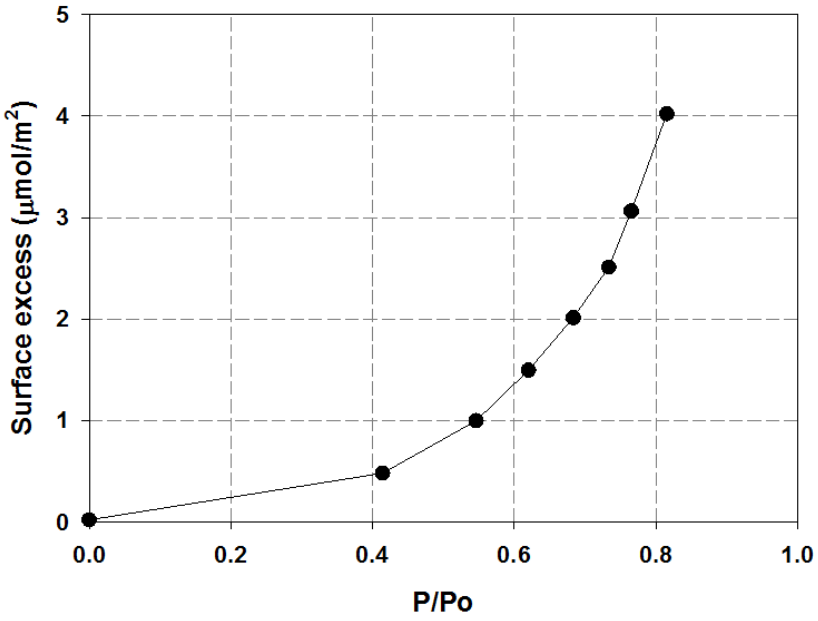


Figure 4: Experimental adsorption isotherm for water on highly graphitised carbon black at 302.15 K [1]

The important features to note here are the Type III isotherm, the low adsorptive capacity, which even at a reduced pressure of 0.8, is considerably less than the amount required to give a statistical monolayer coverage (18.4μmol/m^2) [44]. This convex isotherm has been studied using simulations by Birkett and Do [13] who attached different types of highly attractive functional groups, including localised water molecules on the carbon basal plane, however, their simulated isotherms failed to reproduce the experimental data (shown as unfilled triangles in Figure 5).

Figure 5 presents the simulated adsorption isotherms of water at 302K obtained with our molecular model of the carbon surface, together with the experimental data of Kiselev *et al.* [1] and the simulation results of Birkett and Do [13] for a surface model with four groups of two fixed water molecules. Since the vapour pressure of the SPC/E model is not the same as

the experimental vapour pressure, we have presented these plots in terms of the reduced pressure, i.e. the pressure in the molecular simulation scaled by the vapour pressure obtained from NIST data for SPC/E model (Table 2).

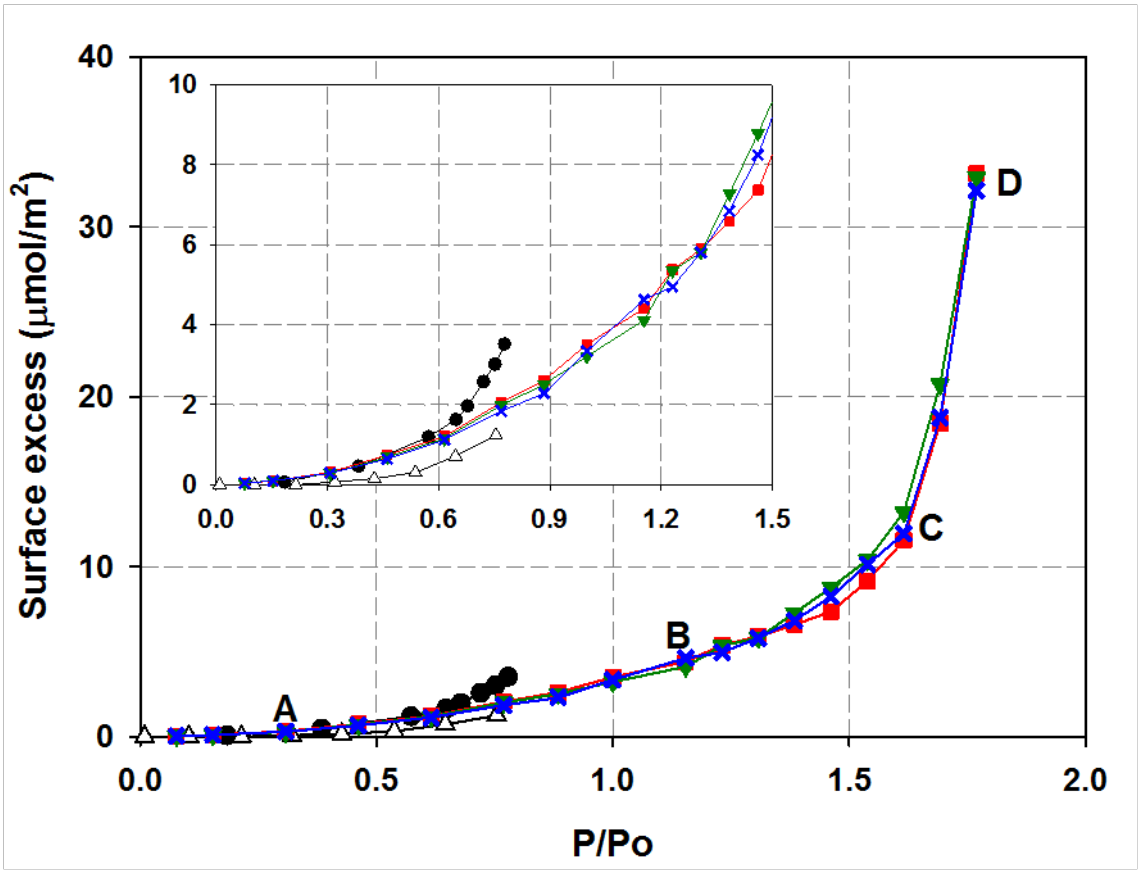


Figure 5: Adsorption of water on the graphite model at 302K. Filled circles represent experimental data [1], unfilled triangles are data taken from Birkett and Do [13], filled rectangles, triangles and crosses are simulation results from this work for different arrangements of phenol groups at the edge sites of graphite. Lines are a guide for the eye only.

Both the experimental and the simulated isotherms in Figure 5 exhibit a gradual increase in the adsorbed amount with pressure. The simulated isotherms obtained in this work are in excellent agreement with the experimental isotherms in the low pressure region (inset of Figure 5). To test our model, we repeated the simulations several times and observed that they all give the same results (shown as filled rectangles, triangles and crosses in Figure 5). As far as we are aware, no previous simulations have been able to fit this experimental data successfully over a period of nearly five decades. When pressure is further increased, the simulated isotherms start to deviate from the experimental one. This can be attributed to the

condensation of water at high pressure in the interstices between the micro-crystallites, which is not accounted for in our molecular model.

In Figure 6 we show snapshots of configurations of water adsorbed on graphite surface at 302K at pressures A-C indicated in Figure 5. At low pressures isolated water molecules are adsorbed onto the phenol groups (snapshot A). The functional groups act as adsorption sites for water adsorption while the bare surface shows no adsorption at low pressure [13] because the potential energy of interaction between water and the graphitic surface is weaker than in the bulk liquid or at the functional groups, where the interaction is dominated by the strong electrostatic contribution to the potential energy. At higher pressures (for example at B) water molecules start to form small clusters around the phenol groups. As the pressure is further increased, these clusters grow gradually and merge with their neighbours to form larger clusters as shown in the snapshot C. The combination of the gradual growth of single clusters and the co-operative merging of clusters as pressure increases is the primary reason for the increase in amount adsorbed resulting in a Type III isotherm.

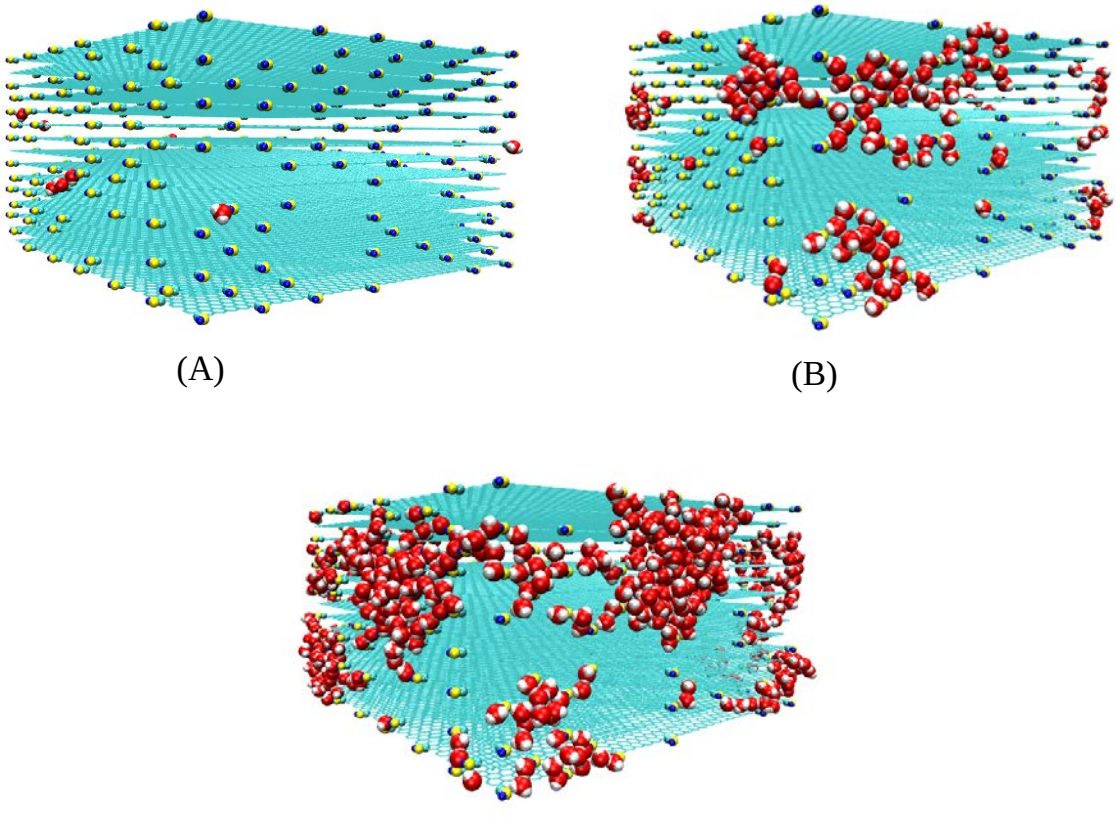


Figure 6: Snapshots of configurations for water adsorption on graphite surface at 302K. Points A-C are indicated on the isotherms in Figure 5

Figure 7 presents the side and top view of the snapshots of water configurations at the pressure indicated as point D in Figure 5. It is seen that water clusters start to merge into one continuous cluster surrounding the solid. Even at these higher pressures, there is no evidence of spill-over of water molecules onto the graphene surface because the hydrogen bonding interaction between water molecules and between water and phenol groups far exceeds the dispersive interaction of water with the graphene surface.

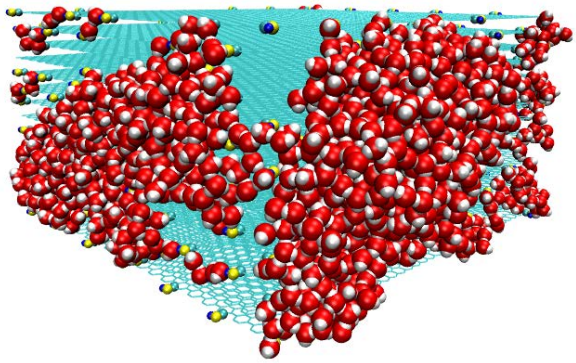
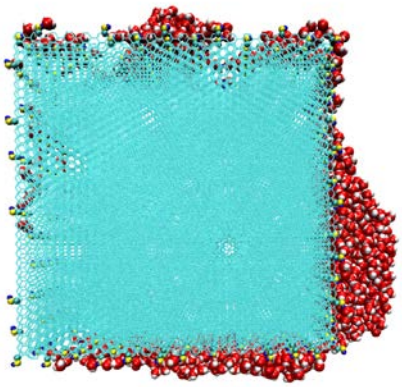
Side view	Top view
	

Figure 7: Snapshots of configurations for water adsorption on graphite surface at 302K (point D indicated in Figure 4)

To further demonstrate the applicability of our model to water adsorption on graphitised carbons, we have carried out simulations at higher temperatures: 313K, 316K and 323K. The results are presented in Figure 8, together with the experimental data of Kiselev and co-workers [1]. Excellent agreement was found between the simulated and experimental isotherms at 313K and 316K, but there is a small deviation for adsorption at 323K at higher loadings, which could be due to the limited space available for water clusters from adjacent micro-crystallites to merge.

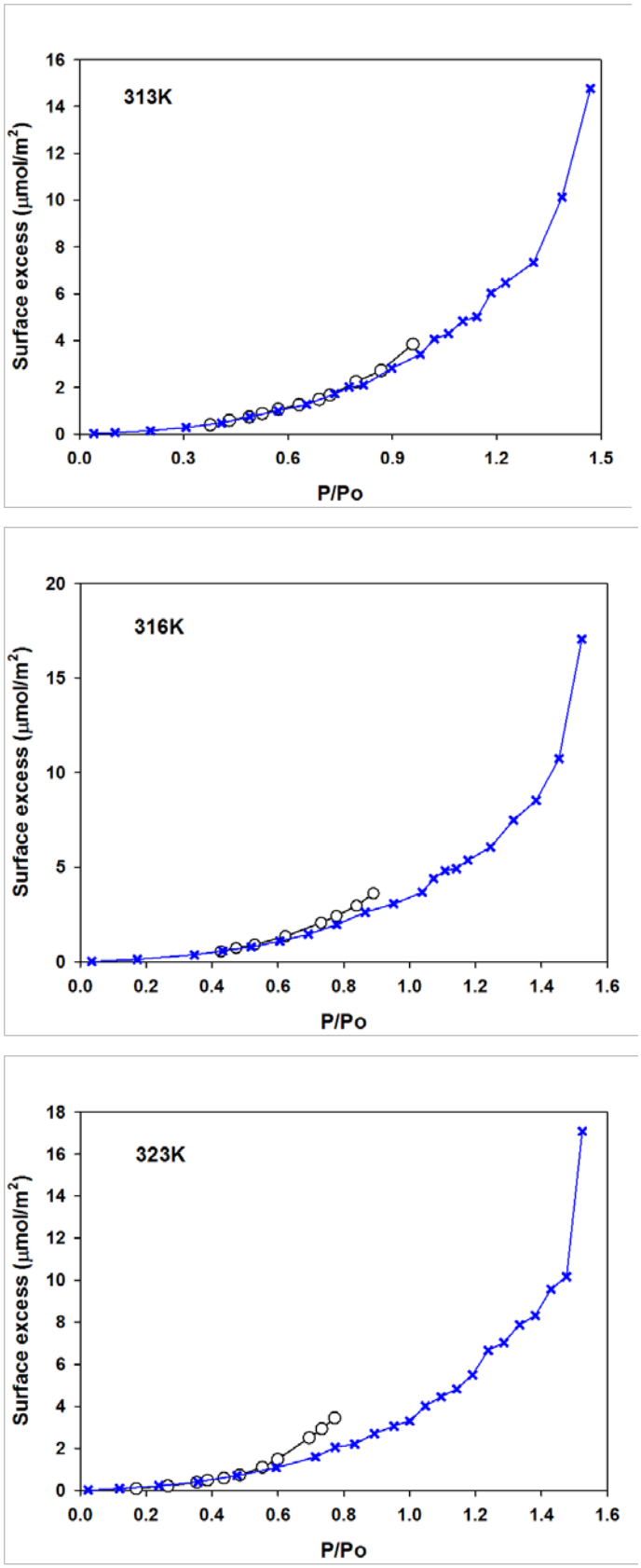


Figure 8: Adsorption of water on graphite surface at various temperatures. Unfilled circles represent experimental data [1] and crosses are simulation results from this work. Lines are guide for the eye only

5. Conclusions

In this paper we propose a new molecular model to describe water adsorption on graphitised carbon black over a range of temperatures. The model is composed of stacked graphene layers with phenolic functional groups forming clusters of various sizes attached at the edges of the graphite. The O/C ratio of the model was equal to 0.006 in close agreement with independent measurements [29]. Simulations were carried out using the SPC/E potential model for water in the grand canonical ensemble. Our molecular model is able, for the first time, to successfully fit the experimental data of Kiselev and co-workers for water adsorption on graphitised carbon over a range of temperatures [1].

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